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Evaluation of a Prototype Field-Portable X-ray Fluorescence System for Hazardous Waste Screening

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EVALUATION OF A PROTOTYPE FIELD-PORTABLE X-RAY FLUORESCENCE SYSTEM FOR HAZARDOUS WASTE SCREENING

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A prototype field-portable X-ray fluorescence system developed by EPA and NASA was evaluated at a site contaminated with Pb, Zn, and Cu. The objective of the field test was to evaluate the effectiveness of the instrument as a field analytical tool for locating hot spots and as a preliminary screening device where immediate data feedback aids in decisionmaking in the field.

By making use of an analytical method designed specifically for the XRF system all routine field measurements for Cu, Zn, and Pb were made on site by placing the probe on the surface of the ground ("in situ" measurements). Subsequently, confirmatory samples were collected and analyzed in the laboratory with an Inductively Coupled Plasma spectrometer (ICP) while adhering to EPA Contract Laboratory Program (CLP) protocols.

The quality assurance consisted of measuring NBS standard reference materials to verify the data measured in the field and in the laboratory in addition to duplicates, blanks, and replicate sample analysis.

The analytical results were plotted on the sampling grid. One can immediately locate the hot spots for Cu, Zn, and Pb on site. The instrument detection limits for Cu, Zn, and Pb are 250, 200, and 70 ppm, respectively. Precision and accuracy of the in situ measurements were within plus or minus 10 percent of the true value when compared to the samples analyzed in the laboratory.

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ABSTRACT

A prototype field-portable X-ray fluorescence system developed by EPA and NASA was evaluated at a site contaminated with Pb, Zn, and Cu. The objective of the field test was to evaluate the effectiveness of the instrument as a field analytical tool for locating hot spots and as a preliminary screening device where immediate data feedback aids in decision-making in the field.

By making use of an analytical method designed specifically for the XRF system, all routine field measurements for Cu, Zn, and Pb were made on site by placing the probe on the surface of the ground ("in situ" measurements). Subsequently, confirmatory samples were collected and analyzed in the laboratory with an Inductively Coupled Plasma spectrometer (ICP) while adhering to EPA Contract Laboratory Program (CLP) protocols.

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The analytical results were plotted on the sampling grid. One can immediately locate the hotspots for Cu, Zn, and Pb on site. The instrument detection limits for Cu, Zn, and Pb are 250, 200, and 70 ppm, respectively. Comparison of the XRF results with the ICP results showed an overall mean percent error (MPE, which means lack of precision and bias incorporated into one term) from NBS concentrations of only a few percent for Cu, Zn, and Pb. Precision and accuracy of the in situ measurements were within plus or minus 10 percent of the true value when compared to the samples analyzed in the laboratory.

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ABBREVIATIONS

AAS	atomic absorption spectrometry
CLP	Contract Laboratory Program
CRDL	contract required detection limits
DI water	deionized water
HF	hydrofluoric acid
HCl	hydrochloric acid
HNO_3	nitric acid
ICP	inductively coupled argon plasma spectrometry
IDL	instrumental detection limit
MPE	mean percent error
NBS	National Bureau of Standards
NPL	National Priority List
ppb	parts per billion
ppm	parts per million
QA/QC	quality assurance/quality control
RSD	relative standard deviation (sample standard deviation divided by the mean times 100)
SRM	standard reference material
XRF	X-ray fluorescence

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SECTION 1

INTRODUCTION

The Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas asked Lockheed Engineering and Management Services Company, Inc. (LEMSCo) to field test and evaluate the performance of a field-portable X-ray fluorescence system for making in situ measurements. In situ measurements are those measurements made by the XRF probe while in direct contact to the ground surface. These measurements are conducted without any sampling and sample preparation other than clearing the ground surface to expose the soil. An in situ XRF measurement represents the data obtained from only the exposed ground surface and does not reflect any of the subsurface. The contaminants in a hot spot would not register a response to the X-rays if the hotspots were covered with as little as 1 cm of uncontaminated soil. Therefore, caution must be exercised in the use of data obtained from in situ measurements. The use of in situ measurements with the XRF system would allow technicians to immediately locate surface hotspots of lead, copper, and zinc on the national priority list (NPL) sites and other sites. The objective of this report is to describe the steps necessary to complete the field test, review the analytical work, and assess the instrumental performance. These steps are as follows:

- design a sound in situ analytical method for a field-portable X-ray fluorescence system prior to the field test
- analyze each of the 40 samples in situ with the field-portable XRF system at 40 locations on a 60 foot by 150 foot grid with sample intervals at every 15 feet.
- subsequently collect confirmatory surface soil samples from the same locations.
- analyze the samples in the laboratory following the ICP CLP protocol (An in situ measurement by a field-portable XRF system has no homogenization technique as a part of sample preparation. The only preparation necessary for an XRF in situ analysis is to clear a flat surface on the soil. Therefore, the sample area of the in situ measurement cannot be considered homogeneous. Acceptance of an in situ XRF measurement dictates the acceptance of a certain amount of error in measurement's accuracy. To validate the in situ XRF measurement, the sample area of the in situ measurement is collected in a volume of sample. The area of the in situ analysis represents one sample and the volume of sample collected represents another. The values of these two samples will closely approximate one another but are technically not the same.

However, the difference in the two values should fall within the acceptance range for the overall inaccuracy of the XRF in situ measurements. For the intents and purposes of this report we will assume the in situ sample area and the collected sample containing the same area to be one and the same sample.)

- compare the XRF results with those obtained from the ICP.

The EPA has recently expressed more interest in XRF systems than in previous years because the use of microprocessors and state-of-the-art technology have made the equipment smaller and thus portable. Such field-portable XRF systems have been used to delineate hazardous waste site hotspots for priority metals in the field (Chappell et al., 1986; Mernitz and Olsen, 1985; Furst et al., 1985; and Kendal et al., 1984). With immediate data feedback from the field-portable XRF system, all samples can be collected with the knowledge of their approximate concentration. This leads to a decrease in the number of unnecessary samples which would be analyzed normally. The XRF field data allows an analyst in the laboratory to calibrate his laboratory instrument to the proper concentration on the first try; thus decreasing the number of attempts at bracketing the correct one. Another use is as a laboratory analytical instrument to screen samples of unknown concentrations quickly providing the analyst with an approximate concentration. All of these applications of the XRF systems net an overall decrease in time and in money spent.

Furst et al., 1985 described three levels of analytical requirements for establishing the extent of environmental contamination. The first or highest level of analysis is used to develop data for litigation and regulatory enforcement (see Figure 1). This level demands the most rigor in sample preparation and instrument time as well as the highest degree of precision and accuracy. The second level of analysis is used to evaluate and assess average contaminant exposures to people and animals. The data from the third level of analysis is used for screening in order to obtain a preliminary profile of sites. This data can be used for decision making while in the field. Third level data may be used also to select which samples should be sent to the laboratory for first level analysis following the Contract Laboratory Program (CLP) analytical protocols. This report discusses the results obtained by using a portable XRF system under the third level of analytical requirements.

The area that the EPA selected for the field test was the Smuggler Mountain NPL site in Aspen, Colorado, northeast of the Aspen city limits. The site was listed on the NPL June 10, 1986. The Smuggler Mountain mine produced lead, silver, and zinc ores. The site is located on one of the slopes of Smuggler Mountain; some of the mining, milling, and smelting was located here. These slopes are a mixture of native soils, mine tailings, and other mine wastes. Much of the surface has been subjected to reworking by prior and recent construction projects. Several such projects used mine tailings as fill.

Martin Marietta Aerospace people brought a prototype XRF system to field test at the Smuggler Mountain site. The first prototype system had evolved from technology used in the Martian Viking lander. This system had to be redesigned to measure metals in contaminated soils because of the changes in its intended usage. Prior to the field test, the software was not programmed

Three Levels of Analytical Requirements for Metals

	Degree of Analytical Requirement			Purpose
	(Precision)	(Accuracy)	(IDL)	
LEVEL I :	Very High			Litigation and Regulatory Enforcement
	(±5%)	(±10%)	(ppb)	
LEVEL II :	Moderately High			Evaluate and Assess Average Pollutant Exposure to Humans and Animals
	(±10%)	(±15%)	(ppm)	
LEVEL III:	Moderate to Low			Screening, Preliminary Evaluation, and On-Site Decision Making
	(±10%)	(±50%)	(≤ ppm x 1000)	

Figure 1. Three levels of analytical requirements for metals.

for efficient evaluation of soil samples and field application. Reprogramming the software took place subsequent to the field test.

The Martin Marietta field-portable XRF system consists of three units (see Figure 2): (1) the sensor head (when filled with liquid N_2, weighs 32 pounds), (2) the Canberra main unit analyzer (16 pounds), and (3) a Gridcase 2 portable computer (12 pounds). The filtration unit shown in Figure 2 was designed for laboratory use only to preconcentrate metals in water samples. The cooled semiconductor detector has excellent energy resolution and is capable of simultaneous detection of a wide range of X-ray energies. The cooled semiconductor detector decreases the dead time response to the X-rays it senses, thus decreasing the length of time needed for analysis. A typical analysis with the system lasts between 120 and 300 seconds. The X-ray tube uses a molybdenum target operating at 30,000 volts to produce a wide enough spectrum to fluoresce the priority elements. The detector is a semiconductor made of lithium drifted silicon. The detector must be cryogenically cooled and must have a continuous supply of liquid nitrogen.

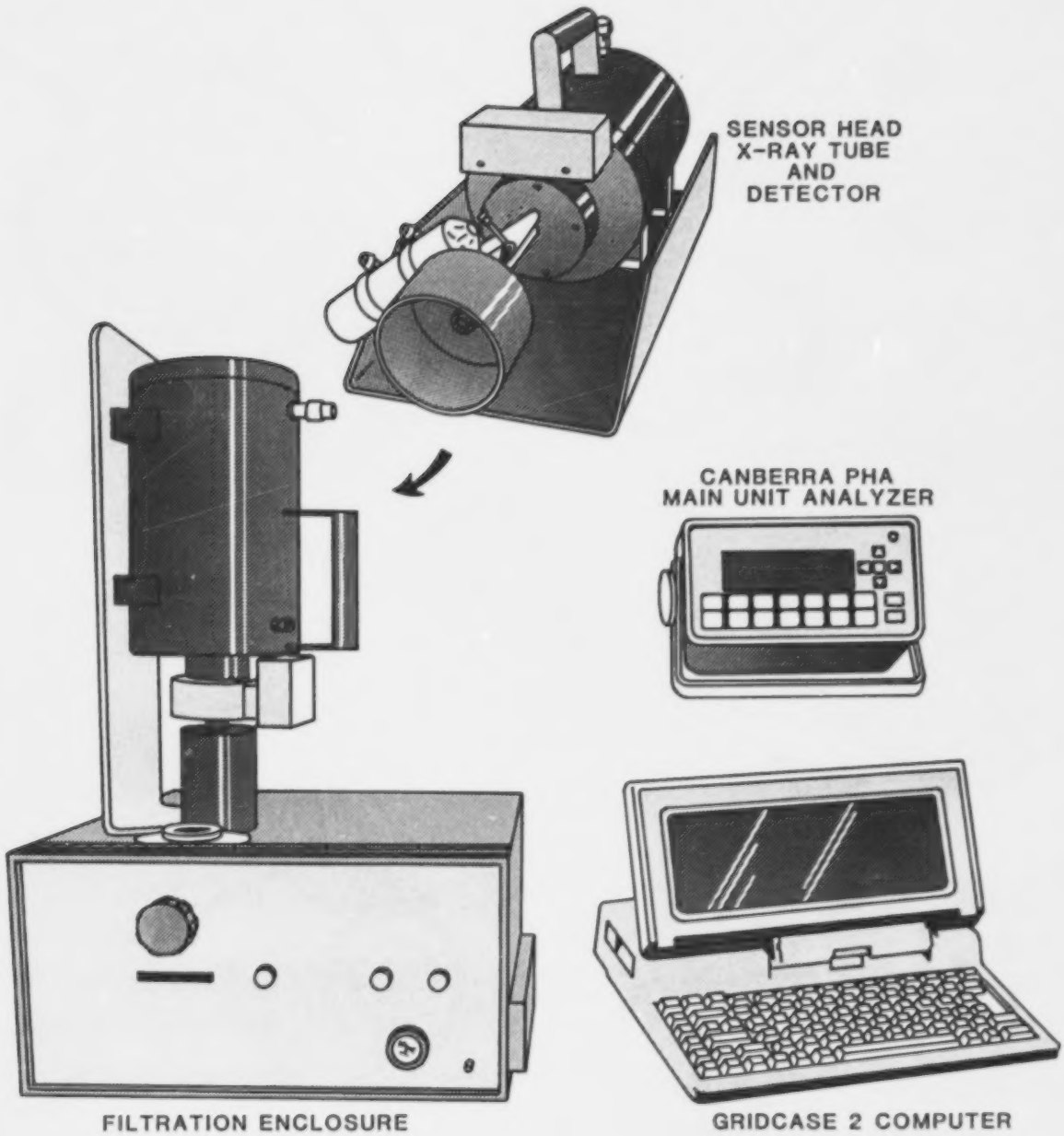

Figure 2. X-ray fluorescence subsystem identification.

SECTION 2

CONCLUSIONS

- The XRF system produced data of known quality from 229 *in situ* measurements (defined as measurements made by placing the probe on the ground surface and by analyzing the same surface without moving the probe). The XRF field results on the NBS standards compared relatively well with the certified NBS values of the same standards.

- Field personnel can greatly decrease the time spent on site by making *in situ* measurements. If necessary, the technician can collect a confirmatory sample after each XRF analysis.

- The detection limits are low enough for obtaining data when third level requirements are necessary for analytical work on hazardous waste site investigations.

- The NBS standards were adequate for quality control and quality assurance. These standards were SRM 1633a, coal fly ash; SRM 1645, river sediment; and SRM 1648, urban particulate.

- The instrument uses cryogenics to cool the silicon-lithium detector which requires a Dewar container filled with liquid nitrogen. Even though the Dewar container will last 8 hours before a refill is necessary, maintaining a continuous supply of liquid nitrogen in the field can be difficult in some locations.

- The overall advantages of all X-ray fluorescent systems include: minimal sample preparation time, rapid turnaround time for analyses, multi-element analytical capability, nondestructive analyses, and sample size required for analysis is small or possibility of surface analysis without the need for sampling at all. These advantages make the XRF system very cost effective.

SECTION 3

RECOMMENDATIONS

- A field methods manual should be written for field XRF measurements and should incorporate field sampling, sample preparation techniques, and analysis.

- Characterized spiked soils should be prepared for the XRF systems as reference standards. These would be spiked at concentrations ranging from 5 to 10 times the IDL, to the highest likely to be encountered; or at levels considered to be a public health hazard.

- A procedure for primary calibration, field update of calibration and of QA/QC checks of the instrument accuracy and precision should be worked out.

- The investigation of a sample preparation method for non in situ measurements should be tested. This should include examination of both the pelletizing and fusing techniques, and the use of loose soil. Indications are that one would obtain different levels of precision.

- The Martin Marietta XRF system should be compared with other commercially available field XRF systems. The detection limits, precision, and accuracy of each instrument could be determined side by side in the laboratory with the ICP or AAS by using rigorous QA/QC protocols, characterized samples, and certified spiked standards.

- Once the instrument detection limits are established for XRF field-portable systems, the initial steps may be implemented in developing these instruments for characterization of uncontrolled hazardous waste sites with respect to specific toxic metals.

SECTION 4

FIELD TEST

Personnel from EPA, Martin Marietta, NASA, LEMSCo, and Camp Dresser and McKee Inc. were present during the field test at the Smuggler Mountain NPL site (Figures 3 and 4). The objective of the field test was to assess the performance of the Martin Marietta field-portable XRF system on an NPL site with regard to effectively identifying hotspots of lead, copper, and zinc. This was accomplished by analyzing *in situ* and by subsequently collecting surface soil samples (see Section 5, Procedures for exact method) on site at 40 locations on a 60 feet by 150 feet grid with sample intervals at every 15 feet (Figure 5). Technicians analyzed each of the 40 samples *in situ* for total Pb, Cu, Zn, and Fe with the field-portable XRF system and processed the data for on site decision making.

NBS standard reference materials (SRM) were used as quality assurance/ quality control standards. The NBS standards were incorporated to give us reference data of known quality. Those used were SRM 1633a, coal fly ash, SRM 1645, river sediment, and SRM 1648, urban air particulate. The NBS standards were analyzed in the field with the XRF system. These values were compared against the SRM-certified values.

A field method was designed specifically for the use of a field-portable XRF system for this field test. This field method is described later under "Analytical Procedures and Sampling Protocol for the Field-Portable XRF System and the ICP." The same samples* were then collected for later confirmatory analysis in the laboratory. To further corroborate the XRF field data, we used the known and accepted CLP methods of preparation and analysis. Because the CLP method of sample preparation uses a relatively weak extraction, we also

*An *in situ* measurement by a field-portable XRF system has no homogenization technique as a part of sample preparation. The only preparation necessary for an XRF *in situ* analysis is to clear a flat surface on the soil. Therefore, the sample area of the *in situ* measurement cannot be considered homogeneous. Acceptance of an *in situ* XRF measurement dictates the acceptance of a certain amount of error in measurement's accuracy. To validate the *in situ* XRF measurement, the sample area of the *in situ* measurement is collected in a volume of sample. The area of the *in situ* analysis represents one sample and the volume of sample collected represents another. The values of these two samples will closely approximate one another but are technically not the same. However, the difference in the two values should fall within the acceptance range for the overall inaccuracy of the XRF *in situ* measurements. For the intents and purposes of this report we will assume the *in situ* sample area and the collected sample containing the same area to be one and the same sample.

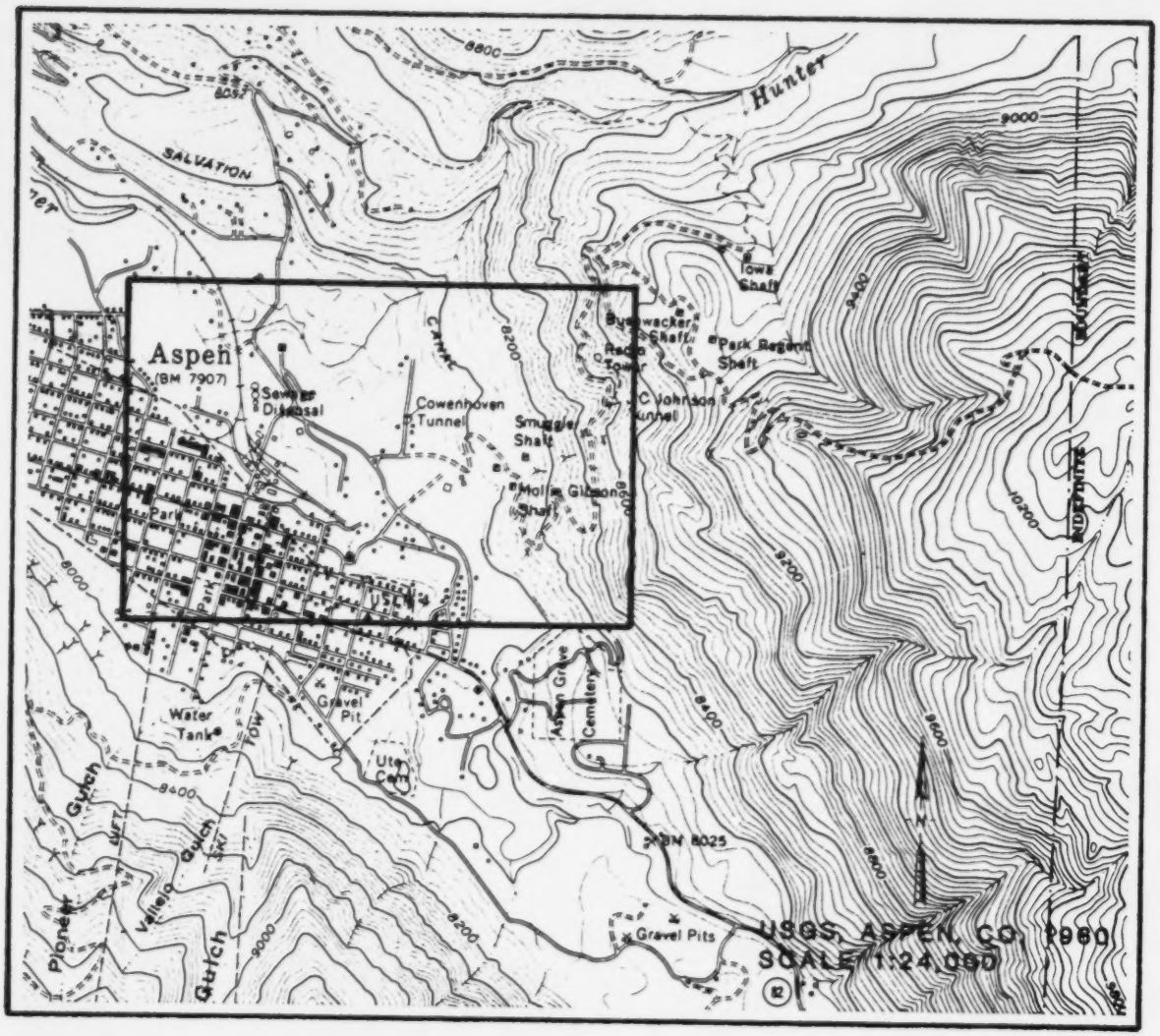

Figure 3. Contour map of Aspen, Colorado.

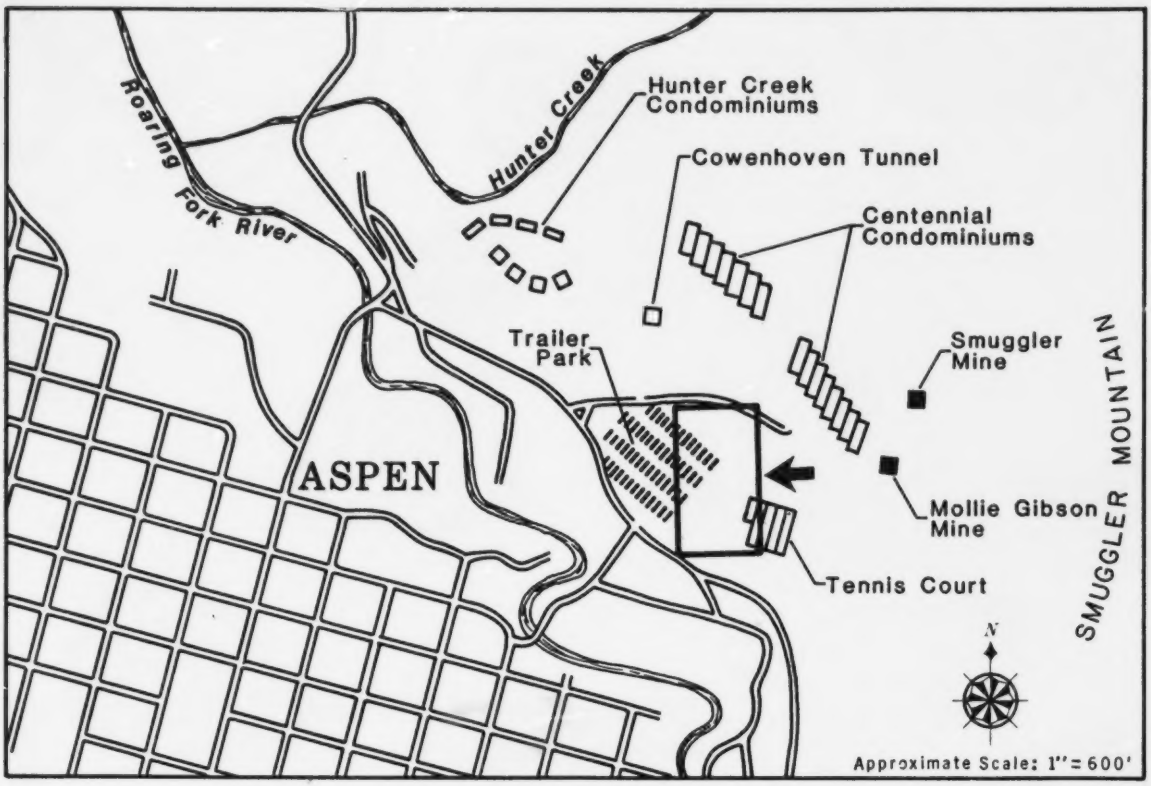

Figure 4. Closer view of site location. Sampling grid is found within the square located by arrow.

used a Parr bomb method to provide a stronger extraction method that was likely to more closely approach the NBS certified values. The Parr bomb method was performed on 13 selected samples but under CLP instrumental requirements for the ICP.

The quality assurance (QA) procedures developed for the XRF field analysis allowed for the proper verification of the data. The verification establishes the quality of the data. To evaluate the reproducibility of measurements (i.e. QA procedures) and to minimize statistical error, the blank, the instrument calibration standard, and the same aliquot from each of the three NBS standards were analyzed seven times each without disturbing the sample.

The results showing high concentrations of Cu, Zn, and Pb on the sampling grids (Figures 6, 7 and 8) can be processed immediately on a computer from the data produced by the XRF system. The capability of immediate analytical results

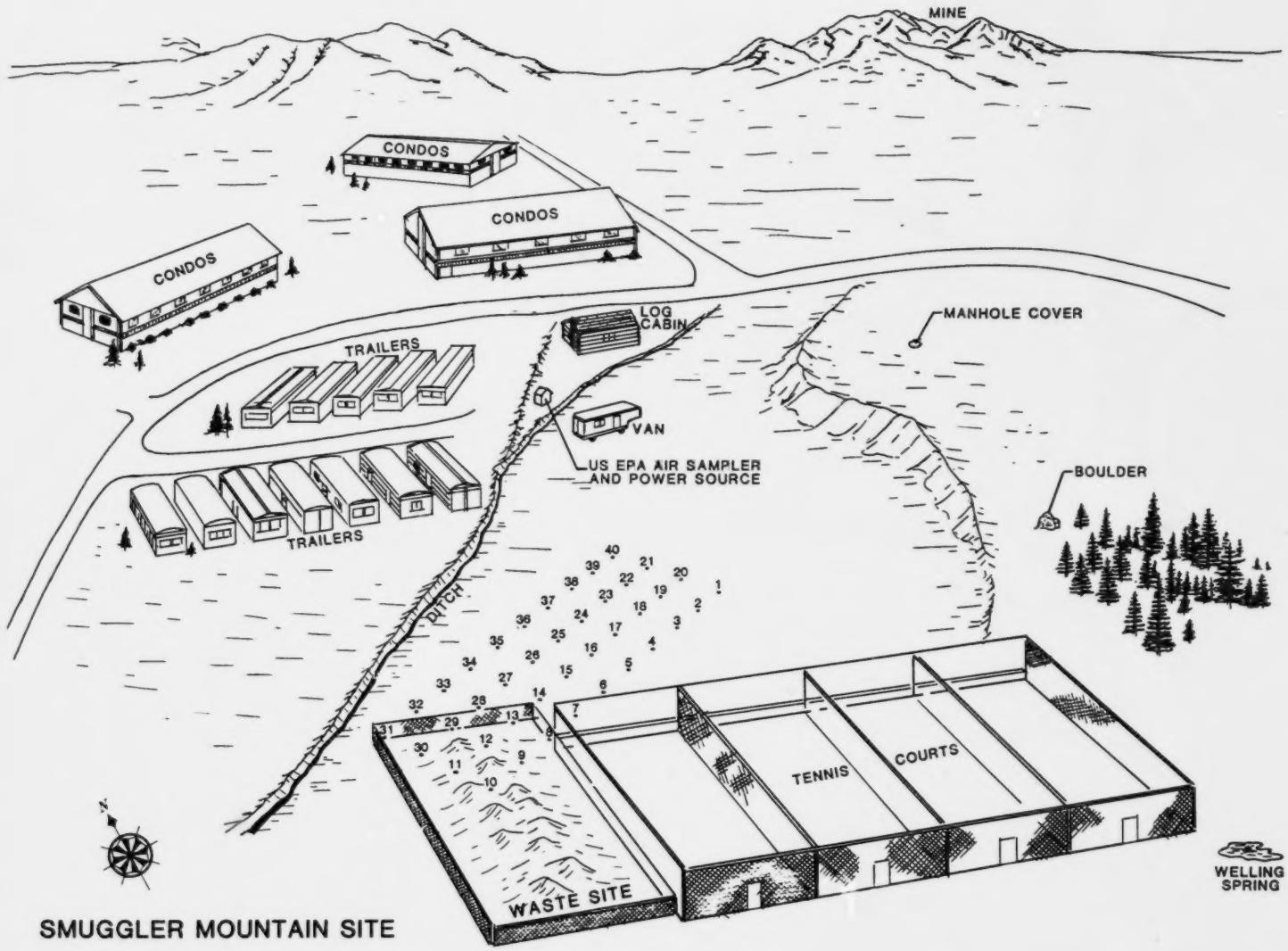

Figure 5. Sampling grid on NPL site.

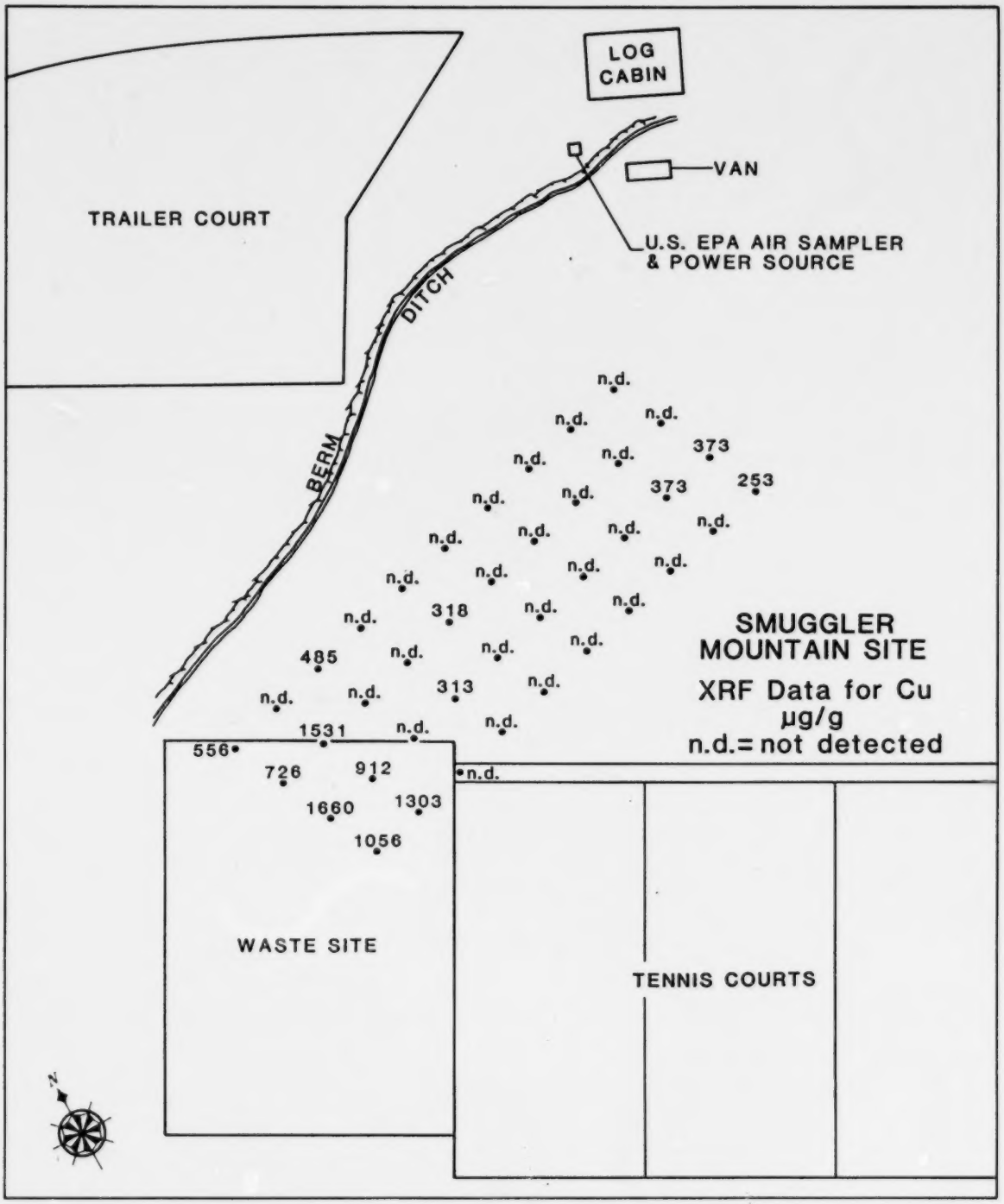

Figure 6. XRF values for Cu plotted on sampling grid.

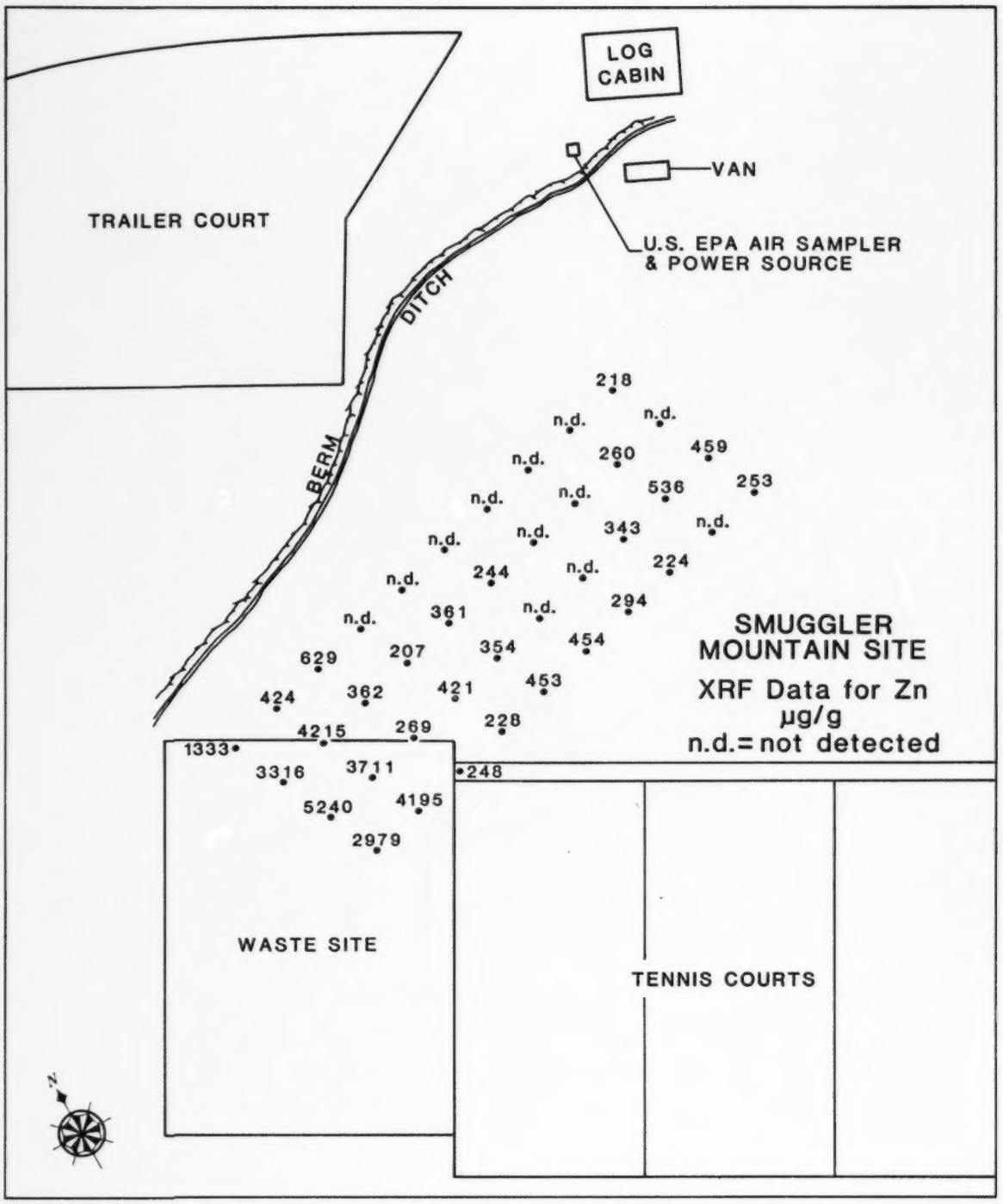

Figure 7. XRF values for Zn plotted on sampling grid.

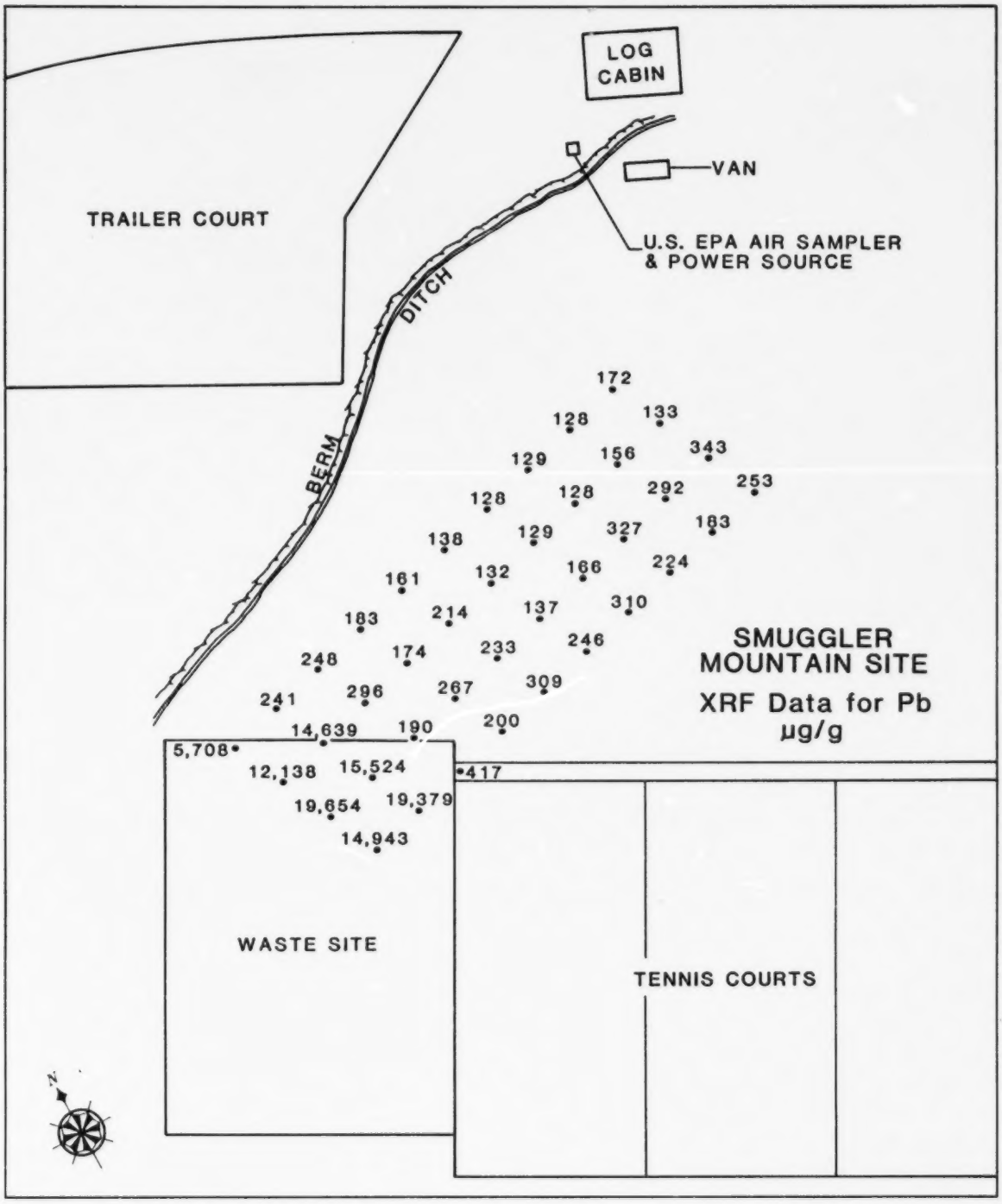

Figure 8. XRF values for Pb plotted on sampling grid.

offers many advantages. The data from the initial screening allows field crews to:

(1) identify the hotspots,

(2) restrict the investigation to the contaminated area,

(3) either go to the next level of investigation or stop at the screening level, and

(4) make decisions based on the data base which is generated from the analyses.

The next level of investigation above screening requires confirmatory samples be taken and analyzed. These can be analyzed in the field. If this were in an area being investigated for the first time, the hotspot would be identified and the locations registering as "background" (non-contaminated) by in situ XRF analysis need not be sampled for confirmation. In our case, the intensified effort would be restricted to the area marked "waste site" in figures 6, 7, and 8. This would decrease the number of samples, which might otherwise be analyzed, and thereby reduce overall analytical costs.

As more samples are analyzed, the data base for the area grows. The initial screening provides the foundation from which the investigation proceeds. The subsequent measurements then provide data of higher quality from which plots can be generated. Field crews can make decisions based on these plots and this data base.

It should be noted that the Martin Marietta XRF field-portable system was required to perform in adverse weather conditions. It began snowing during the field test and the XRF system did not malfunction. The authors feel that the system performed well under these conditions.

SECTION 5

PROCEDURES

X-RAY FLUORESCENCE PRINCIPLES

The X-ray fluorescence (XRF) system used in this study is energy dispersive by design. All XRF depends on either an electron or X-ray beam bombarding the sample. The X-rays produced by an X-ray tube impinge on the electron clouds or orbitals in the atoms within the sample. When the X-ray displaces an electron from an inner orbital of an atom, such as the k-shell, a vacancy is created. This causes an instability below the electrons in outer shells. As the outer electrons seek stability by filling the inner shell vacancies, a cascade of electrons spontaneously follows. Energy is released or emitted for each shell vacancy that is filled. This emitted energy is characteristic of the atom from which it was produced. This emission is called fluorescence. All elements excited by the X-rays fluoresce simultaneously to produce a spectrum of characteristic and backscattered radiation. It is this spectrum that the detector senses and counts. The whole spectrum data is transferred to the analyzer where the software deconvolutes the peaks for the desired elements.

THE PROBLEM OF RESOLUTION WITH VARYING PARTICLE SIZE

The bulk density of the sample and the particle size distribution affect the characteristic X-ray intensity. When dealing with varied distribution of particle sizes, an accurate analysis of these particles is difficult if there is no attempt to make all the particles the same size, either by segregation or reduction.

The varied particle sizes have an effect on X-ray absorption and enhancement especially during in situ emission analysis. Collecting and grinding the sample to <0.075-mm (200 M) will generally solve the problem, but this is not always a practical solution in the field. It also defeats the purpose of using the field-portable XRF system with an in situ technique, i.e., a fast turnaround time. We can address this problem in a sample preparation step by using a mortar and pestel to break up the soil samples and by grinding the sample to approximately sand size assuming the sample is dry. Even though this approach does not entirely solve the problem, it does reduce the effect to an acceptable constant error while keeping sample preparation time to a minimum.

ANALYTICAL PROCEDURES AND SAMPLING PROTOCOL FOR THE FIELD-PORTABLE XRF SYSTEM AND THE ICP

Field personnel analyzed and collected 40 soil samples according to the following method:

XRF Analysis:

a. The analyst will make seven replicate measurements, rotate the sample 90°, stir each standard, and make seven more replicate measurements on the following:

   - a blank sample made of silica sand,
   - the instrument calibration standard,
   - the three NBS standards.

b. Clear the area for analysis by removing rocks and debris from the surface, mark the area, place the instrument on the designated area, and activate the X-rays.

c. The analyst will make single measurements on the following:

   - the soil sample,
   - a standard with concentrations closest to the soil values,
   - the instrument calibration standard.

d. The analyst will make a duplicate analysis on every tenth soil sample without moving the probe.

e. Record all data pertinent to the sample, its location in a logbook, and store the analytical data obtained from the instrument on a diskette.

f. After the analyst finishes measuring the soil sample in situ, collect the sample for later corroborative analysis.

g. Collect the sample using the following steps:

   - Use a clean trowel to take a 200 cc sample. Penetrate a 2" x 2" area on the surface to no more than 2 inches deep. Be sure to include the area which has been analyzed in situ.
   - Empty the sample into an acid-washed 150 mm x 25 mm plastic petri dish, being sure to fill the petri dish to approximately two-thirds full, seal the petri dish inside a plastic zip-lock bag, and seal the bag with tape.

- Clean the trowel by wiping the blade with a paper towel and then rinsing with distilled water.

h. Take samples with contamination levels ranging from approximately five times the IDL for Cu, Zn, and Pb up to the maximum values found on site.

i. Use NBS standards for the reference calibration.

j. Use silica sand for the blank sample. The grains of silica sand will closely approximate the grain geometry of the soils.

The sample preparation for the ICP analyses was done by both the standard CLP method and the Parr bomb method which is described below. The CLP method and QA/QC protocol for analysis may be found in Exhibit D of the Invitation for Bid for the Contract Laboratory Program (U.S. EPA, 1984).

ICP Analysis

Digestion of soil by a generic Parr bomb method (adapted from Bernas, 1968, Buckley and Cranston, 1971; and Dolezal et al., 1969):

a. Dry at 60°C and homogenize the sample.

b. Weigh 0.5 g of soil and place it in the Parr bomb.

c. Add 5 mL of concentrated nitric acid (HNO_3) and 2 mL of concentrated hydrochloric acid (HCl).

NOTE:
- Do not add more than the 2 mL HCl prescribed. Too much can generate enough chlorine gas to cause the Parr bomb to explode.
- Do not add any soil with carbonates; the evolution of CO_2 could cause the Parr bomb to explode.
- Do not add the filter paper if it is a cellulose base. This could cause the formation of nitrocellulose which is explosive.

d. Seal the Parr bomb and place it in an oven at 120°C for 2 hours.

e. Remove the bomb from the oven and allow it to cool to room temperature.

f. Open and rinse the contents into a filter funnel feeding into a 100-mL volumetric flask. Bring the flask up to volume with DI water. The digest is ready for analysis.

SECTION 6

RESULTS AND DISCUSSION

DISCUSSION OF SOFTWARE

The application of the XRF system changed throughout its development, and the programming of the software did not keep pace. The software was not modified for field use or for soils analysis prior to the first field test. For the field test at Smuggler Mountain, the XRF system was calibrated in the laboratory with spiked soils for the metals of interest and was checked against certified NBS standards, but the software was set up for metal alloys. The data and the samples were collected in the field. Then the data was taken back to the Martin Marietta where the software was reprogrammed to process the data for field use and soils analysis.

The software program for peak deconvolution caused many of the non-priority metals to drop out. While beyond the scope of this study, the authors feel that the software should be investigated to optimize the deconvolution of the peaks.

COMPARISON OF XRF RESULTS VERSUS ICP (Parr bomb and CLP) RESULTS

To evaluate the performance of the field-portable XRF system, technicians analyzed the NBS standards and 40 soil samples from Smuggler Mountain on a Perkin Elmer ICP II by using two sample preparation methods. The first preparation method is an extraction procedure (Parr bomb described previously) and the second preparation method is the standard CLP instrument extraction procedure. Technicians analyzed the Parr bomb digest also according to CLP instrument requirements. We did not use a total dissolution procedure because most such procedures use hydrofluoric acid (HF). It is necessary to neutralize the HF with large quantities of boric acid. The high amount of dissolved solids tends to clog the nebulizer, thus affecting precision by causing drift.

The analytical results of the NBS standard reference materials (SRM) for four metals by XRF and ICP (both methods) are listed in Table 1. EPA requested that Pb, Cu, and Zn be examined. We added Fe to show how the XRF unit responded to a constant high value while analyzing the other metals in varying amounts.

When we compare the values overall, the XRF analyses tend to be higher than the ICP analyses. The analysis of the urban particulate, SRM 1648, showed the best results. The XRF results are between 95 percent and 105 percent of what the NBS has certified as present in the SRM 1648 with the exception of Zn. Since Martin Marietta designed the XRF system as a semi-quantitative instrument for the field, these analyses are excellent within the limitations of the

TABLE 1. COMPARISON OF XRF AND ICP RESULTS FROM NBS STANDARDS

	Analysis Number	Elements Fe	Cu	Zn	Pb
		(all units are in ug/g)			
		Coal Fly Ash			
SRM 1633a	1	94,000	118	220	72.4
	2	91,555	178	261	152.4
	3	38,780	75.6	103	34.4
	4	17,944	54.0	84	n.a.
		River Sediment			
SRM 1645	1	113,000	109	1720	714
	2	313,686	183	1551	735
	3	84,410	109	1632	688
	4	n.a.	n.a.	n.a.	n.a.
		Urban Particulate			
SRM 1648	1	39,100	609	4760	6550
	2	41,252	584	2212	6247
	3	21,746	550	4486	5986
	4	20,857	432	3443	4192

No. 1 Certified by National Bureau of Standards.
No. 2 Martin-Marietta XRF unit. The Martin Marietta values for the SRM 1633a and 1648 are the averages of 7 replicates; for the SRM 1645, the values are the averages of 14 replicates.
No. 3 Perkin Elmer ICP II, Parr Bomb Method. The values are the averages of 3 replicates.
No. 4 Perkin Elmer ICP II, CLP Methods. The values are the averages of 3 replicates.
n.d. = not detected.
n.a. = not analyzed.

standards. When the individual Pb values for the different standards from Table 1 are plotted, the XRF results of the NBS standards show excellent concurrence with the ICP, especially for Pb (Figure 9).

The detection limits for the XRF system were determined by Martin Marietta. Three 300-second spectra were collected for each element, and the ratios of the net Kα and Lα peaks to net backscatter calculated. The instrumental detection limit was calculated from the formula:

$$IDL = 3S\sqrt{C_b/C_s}$$

where S is the quantity (in micrograms) of metal present in the sample, C_b is the background counts under the peak, and C_s the net sample counts. The peak

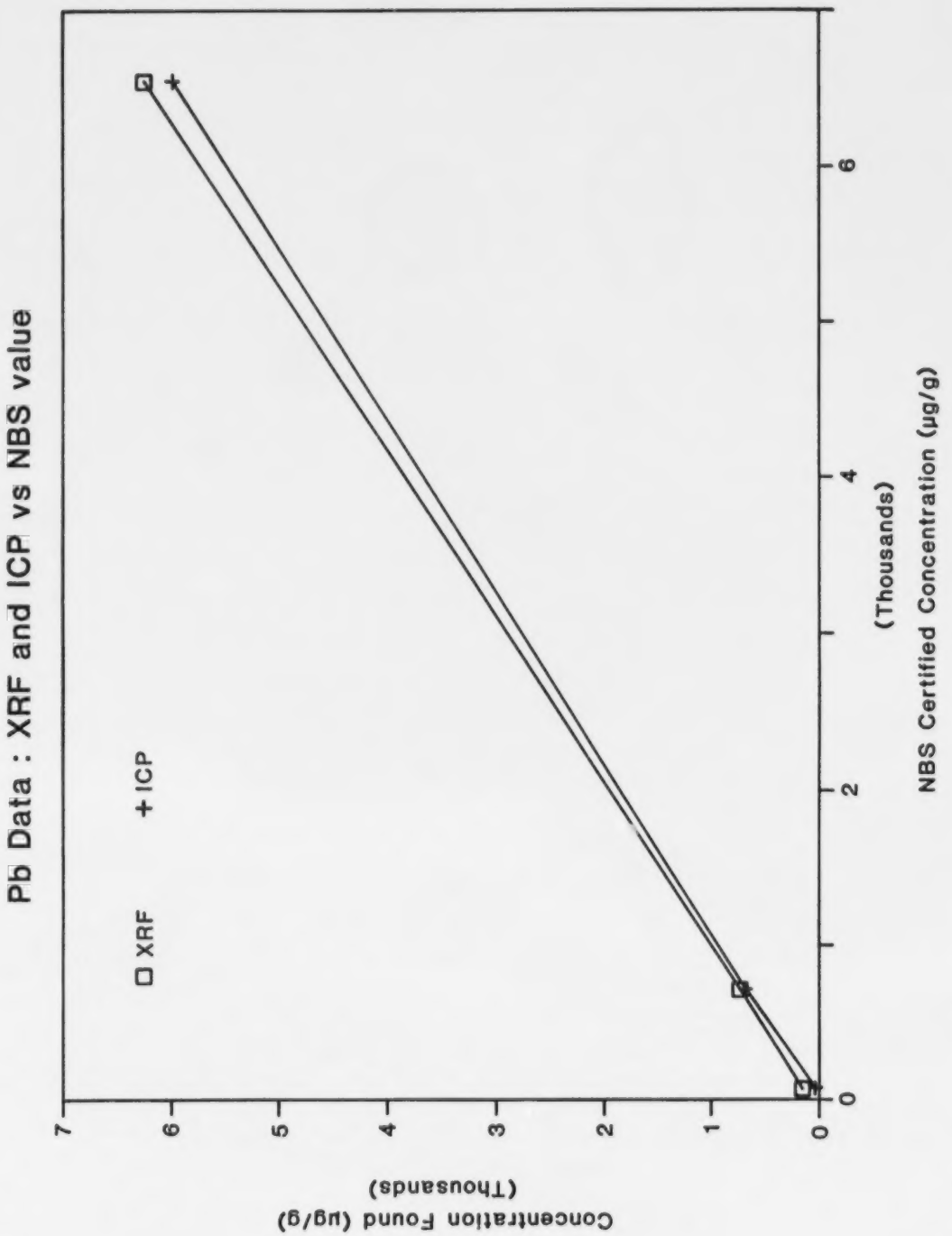

Figure 9. XRF and CLP results versus NBS certified concentrations.

TABLE 2. COMPARISON OF THE MARTIN MARIETTA XRF SYSTEM AND THE ICP INSTRUMENT DETECTION LIMITS AGAINST CLP CONTRACT REQUIRED DETECTION LIMITS (CRDL)

Element	Martin Marietta XRF System[1] (ppm)	Perkin Elmer ICP[2] (ppb)	ICP CRDL (ppb)
Cu	250	8	25
Pb	70	35	(5)*
Zn	200	17	20
Cr	1000	5	10
Ni	300	30	40
As	150	80	(10)*
Se	140	170	(5)*
Ag	>1000	5	10
Cd	ND	4.8	5
Sb	ND	50	60
Ba	>1000	20	200
Hg	80	50	(0.2)*
Tl	75	160	(10)*

1 Data provided by Martin Marietta.
2 IDL's qualified for CLP.
* These metals are not required for analysis on the ICP under CLP protocols. The values in the parentheses are the measured IDL's for the atomic absorption spectrometer to show its capability.
ND = not detected.

background is calculated, and the net sample counts are calculated by subtracting the background level from the total number of counts in the peak. The detection limits for the XRF (the IDL for iron was not included) and ICP instrumental detection limit (IDL's) are listed in Table 2 and are compared in the CLP contract required detection limits (CRDL). The CRDL's represent a level one requirement regime for analytical work. The XRF IDL's might represent a proposed level three requirement regime for hazardous waste site investigations with field-portable XRF systems.

In comparison of the IDL's for Cu, Zn, and Pb against the values for the soil samples in Table 3, what immediately becomes apparent is that 29 of the values for Cu measured by the Martin Marietta XRF system are less than or equal to the instrumental detection limit. Any values below five times the IDL should not be used. The variation of precision in this range is, as a rule of thumb, plus or minus the IDL. Between 5 and 10 times the IDL, the variation in precision ranges from 10 percent to 20 percent of the amount present. Above 10 times the IDL, the variation in precision is less than 10 percent of the amount present.

TABLE 3. COMPARISON OF XRF AND ICP RESULTS FROM SOIL SAMPLES

Sample No.	Analysis No.	Elements			
		Fe	Cu	Zn	Pb
		(all units are in mug/g)			
G-1	1	25,511	253	323	253
	2	n.a.	n.a.	n.a.	n.a.
	3	13,461	17.1	364.9	315.1
G-2	1	23,396	b.d.l.	232	183
	2	n.a.	n.a.	n.a.	n.a.
	3	15,669	27.5	374.3	282.2
G-3	1	24,114	b.d.l.	257	224
	2	n.a.	n.a.	n.a.	n.a.
	3	19,016	20.6	434.3	416.3
G-4	1	33,460	n.d.	294	310
	2	n.a.	n.a.	n.a.	n.a.
	3	17,331	18.7	410.6	356.4
G-5	1	32,159	b.d.l.	454	246
	2	n.a.	n.a.	n.a.	n.a.
	3	14,460	15.7	323.6	342.3
G-6	1	43,749	b.d.l.	453	309
	2	n.a.	n.a.	n.a.	n.a.
	3	15.596	18.6	369.0	301.1
G-7	1	22,317	b.d.l.	228	200
	2	n.a.	n.a.	n.a.	n.a.
	3	16,872	17.7	442.7	503.5
G-8	1	21,237	n.d.	248	417
	2	19,410	59.8	1,617.3	3334.0
	3	13,359	22.9	676.1	1234.5
G-9	1	70.532	1,303	4,195	19,379
	2	23,758	55.3	4,517.6	11,492
	3	27,119	67.8	6,042.5	11,791
G-10	1	57,729	1,056	2,978	14,943
	dup	52,947	919.1	3,022.2	14,840
	2	32,620	100.0	6,544.6	18,539
	3	27,259	73.4	6,134.8	12,875

Footnotes at end of table.

(continued)

TABLE 3. (Continued)

Sample No.	Analysis No.	Elements Fe	Cu	Zn	Pb
		(all units are in ug/g)			
G-11	1	82,978	1,660	5,240	19,654
	2	23,422	42.4	5,265.9	11,615
	3	36,969	80.7	9,383.5	15,294
G-12	1	52,830	912	3,711	15,524
	2	27,606	77.8	6648.4	11,619
	3	26,673	102.7	6347.0	4,135.1
G-13	1	30,009	174	269	190
	2	11,405	13.0	241.9	165.1
	3	12,413	14.2	263.5	176.1
G-14	1	39,972	313	421	267
	2	n.a.	n.a.	n.a.	n.a.
	3	15,099	17.1	344.1	226.8
G-15	1	38,180	208	354	233
	2	n.a.	n.a.	n.a.	n.a.
	3	14,157	15.9	293.6	176.9
G-16	1	35,277	163	168	137
	2	n.a.	n.a.	n.a.	n.a.
	3	21,159.3	23.2	102.7	19.1
G-17	1	35,331	151	153	166
	2	n.a.	n.a.	n.a.	n.a.
	3	25,141	27.2	243.6	137.6
G-18	1	31,529	158	343	327
	2	n.a.	n.a.	n.a.	n.a.
	3	17,234	22.3	422.5	327.6
G-19	1	39,512	373	536	292
	2	n.a.	n.a.	n.a.	n.a.
	3	15,069	21.8	451.3	812.7
G-20	1	38,321	373	449	343
	dup	33,990	304.3	417.0	281.9
	2	n.a.	n.a.	n.a.	n.a.
	3	14,003	21.4	459.3	396.2

Footnotes at end of table.

(continued)

TABLE 3. (Continued)

Sample No.	Analysis No.	Elements Fe	Cu	Zn	Pb
		(all units are in ug/g)			
G-21	1	45,242	b.d.l.	b.d.l.	133
	2	n.a.	n.a.	n.a.	n.a.
	3	22,018	23.6	102.0	15.4
G-22	1	36,814	b.d.l.	260	156
	2	n.a.	n.a.	n.a.	n.a.
	3	14,868	18.9	329.2	436.6
G-23	1	36,202	n.d.	165	121
	2	n.a.	n.a.	n.a.	n.a.
	3	20,862	22.9	124.5	32.9
G-24	1	38,416	n.d.	b.d.l.	129
	2	n.a.	n.a.	n.a.	n.a.
	J	21,580	24.4	165.3	61.5
G-25	1	33,462	n.d.	244	132
	2	n.a.	n.a.	n.a.	n.a.
	3	20,231	22.5	111.7	17.3
G-26	1	28,503	318	361	214
	2	n.a.	n.a.	n.a.	n.a.
	3	14,765	20.1	390.2	281.3
G-27	1	31,856	b.d.l.	207	174
	2	n.a.	n.a.	n.a.	n.a.
	3	13,543	18.9	388.5	212.5
G-28	1	37,600	b.d.l.	362	296
	2	12,813	15.0	275.8	194.2
	3	14,903	20.5	375.7	314.6
G-29	1	56,334	1,531	4,215	14,639
	2	22,712	68.8	4,315.7	6,833
	3	26,774	90.9	8,467.3	8,924
G-30	1	57,050	726	3,316	12,138
	dup	58,350	742.9	3,489.6	11,927
	2	25,613	73.8	4,497.4	8,031
	3	20,075	81.4	4,780.1	7,235

Footnotes at end of table.

(continued)

TABLE 3. (Continued)

Sample No.	Analysis No.	Elements Fe	Cu	Zn	Pb
		(all units are in ug/g)			
G-31	1	47,989	556	1,332.5	5,707.9
	2	25,092	68.0	5,347.1	7,090.8
	3	27,010	79.9	6,164.1	1,016.3
G-32	1	34,662	b.d.l.	424	241
	2	9,521	11.4	234.5	240.6
	3	9,897	11.2	253.4	269.4
G-33	1	29,650	485	629	248
	2	7,902	8.4	175.3	159.6
	3	12,007	13.9	282.6	255.4
G-34	1	20,454	b.d.l.	b.d.l.	183
	2	46,904	41.3	209.8	178.5
	3	9,916	11.2	244.2	164.3
G-35	1	21,212	n.d.	b.d.l.	161
	2	n.a.	n.a.	n.a.	n.a.
	3	14,970	17.2	366.1	286.4
G-36	1	37,457	n.d.	b.d.l.	138
	2	n.a.	n.a.	n.a.	n.a.
	3	25,310	37.5	143.5	47.8
G-37	1	40,321	b.d.l.	b.d.l.	128
	2	n.a.	n.a.	n.a.	n.a.
	3	20,846	19.4	119.0	43.9
G-38	1	35,042	n.d.	b.d.l.	129
	2	n.a.	n.a.	n.a.	n.a.
	3	21,7α0	20.8	180.2	100.2
G-39	1	36,218	b.d.l.	b.d.l.	128
	2	n.a.	n.a.	n.a.	n.a.
	3	24,390	21.5	108.5	28.7

Footnotes at end of table.

(continued)

TABLE 3. (Continued)

Sample No.	Analysis No.	Elements Fe	Cu	Zn	Pb
		(all units are in ug/g)			
G-40	1	27,283	b.d.l.	218	172
	dup	30,954	n.d.	94.9	151.7
	2	n.a.	n.a.	n.a.	n.a.
	3	15,246	16.5	324.0	456.3

No. 1 Martin-Marietta XRF system.
No. 2 Perkin Elmer P-2 ICP, Parr bomb method.
No. 3 Perkin Elmer P-2 ICP, CLP methods.
dup = duplicate analysis of No. 1.
n.d. = not detected.
n.a. = not analyzed.
b.d.l. = below detection limit.

When a sample is wet, the bulk density changes, greater absorption of X-rays takes place, and the XRF values are lower. Compounding the absorption effect are the grain geometry and particle size distribution which also affect the absorption of X-rays (Rhodes and Hunter, 1972). These uncontrolled parameters account for some of the XRF results which are lower than the CLP results throughout Table 3.

Some 13 samples were selected to be analyzed by the Parr bomb method. Although the Parr bomb method is a strong extraction procedure, the nitric and hydrochloric acid extract did not dissolve all the metals beeause the silicates are not soluble in these acids. The silicates often entrap some of the metals within them. The CLP method is simply an HNO_3 extraction procedure, and thus, we expect the recoveries to be lower than a total dissolution or XRF analysis. The XRF analysis is comparable to a total dissolution in that the measured response of the fluorescence accounts for all elements with an atomic number greater than Z = 9 up to Z = 92. This range covers most elements occurring in a natural soil even with contaminants.

A problem developed with use of the Parr bomb while analyzing SRM 1633a and 1645. The addition of 2 mL of HCl caused the generation of too much Cl_2 gas. The Parr bomb was not sealed tightly enough and allowed the pressure to vent. This leakage strongly affected some of the Parr bomb results and accounts for the Parr bomb values for routine samples being less than the CLP values in Table 3, especially with reference to the iron results. The iron combines with the chlorine to form iron chloride which is volatile at 120°C and leaked out with the Cl_2 gas. The standards SRM 1633a and 1645 were reanalyzed, and the following changes were made: the sample amount was changed to 0.25 g, the amount of HNO_3 was changed to 3 mL, and HCl was changed to 0.5 mL; and special attention was given to the sealing of the Parr bomb itself. The results show that the reanalysis of SRM 1645 recovered concentrations very close to the NBS certified concentrations. Recoveries for SRM 1633a, the coal fly ash, show low

concentrations but they are still closer to the NBS certified concentrations than the CLP recovered concentrations.

COMPARISON OF TWO FIELD-PORTABLE XRF SYSTEMS

We sent 13 soil samples to the Kevex Corporation for analysis with their field-portable XRF system, X-site 9900 and Analyst 6700. Kevex agreed to analyze the samples at no cost. Because Kevex analyzed these samples without contractual requirements the analyses were not verifiable. Therefore, the data must be accepted only as approximate values. In spite of this deficiency, we gain enough insight from the data to warrant its inclusion here (Table 4). The samples were shipped as loose soils sealed in petri dishes. Kevex analyzed the samples by placing the probe of their x-site 9900 onto the samples in the petri dishes. No sample homogenization or preparation took place. Overall the Fe values of the two instruments are close enough for semi-quantitative work, but the values for the priority metals Cu, Zn, and Pb are diverse for the two instruments and need further investigation. The authors suggest that further comparative work in the laboratory with rigorous QA/QC would determine which XRF system is better suited for field work.

STATISTICS

The replicate precision on the standards of the Martin Marietta XRF system ranged from 1.2 percent RSD for Zn to a maximum of 34.4 percent RSD for Pb on the NBS SRM 1648 (Table 5). The second column for each element represents the 90° rotation in the same horizontal plane after the seven-replicate analysis. The difference in the two sets of analyses could reflect the effect due to surface morphology from different areas within a sample which can affect the X-rays the detector senses.

The duplicate precision on routine samples of the Martin Marietta XRF system ranged from 0.88 percent RSD to a maximum of 10.19 percent RSD on the three samples run (Table 6). The relatively high percent RSD's which appear with sample G-20 could occur due to the counting statistics and being close to the instrument's detection limit. The more controlled studies need to be done in this area.

In Figure 10, the bar graph is a plot of the percent relative root mean square deviation verses the elements Fe, Cu, Zn, and Pb for each method. The data from Table 1 was used to calculate the mean percent error (MPE) using the formula:

$$MPE = \sum_{i=1}^{3} \frac{|X_i - T_i|}{3T_i} \times 100$$

where:

X_i = recovered concentration for a method
T_i = NBS certified concentration

TABLE 4. COMPARISON OF TWO FIELD PORTABLE XRF SYSTEMS

Sample No.	Analysis No.	Elements (all units are in ug/g) Fe	Cu	Zn	Pb
G-1	1	25,511	253	323	253
	2	25,052	111	n.d.	220
G-3	1	24,114	b.d.l.	257	224
	2	29,473	n.d.	64	268
G-7	1	22,317	b.d.l.	228	200
	2	24,326	45	n.d.	536
G-14	1	39,972	313	421	267
	2	28,127	n.d.	175	340
G-16	1	35,277	b.d.l.	b.d.l.	137
	2	22,019	n.d.	n.d.	n.d.
G-19	1	39,512	373	536	292
	2	33,488	n.d.	670	453
G-22	1	36,814	105	260	156
	2	30,882	n.d.	n.d.	621
G-25	1	33,462	n.d.	244	132
	2	36,179	n.d.	n.d.	268
G-27	1	31,856	b.d.l.	207	174
	2	32,121	171	n.d.	302
G-31	1	47,989	556	1,333	5,708
	2	30,904	n.d.	4,873	6,028
G-34	1	20,454	174	198	183
	2	22,339	52	422	275
G-37	1	40,321	39	103	128
	2	39,575	230	8,704	11,427

No. 1 Martin-Marietta XRF.
No. 2 Kevex Corporation XRF.
n.d. = not detected.
b.d.l. = below detection limit.

TABLE 5. REPLICATE ANALYSES OF THE NBS SRM 1648
(Data supplied by Martin Marietta)

Flux Factors	Gross backscatter (counts per second) Fe X100	Fe X100	Zn X1000	Zn X10	Pb X1000	Pb X10
A-1	3.464	6.150	2.818	1.853	5.795	1.563
A-2	3.289	5.999	2.203	1.854	2.870	1.629
A-3	3.225	5.909	2.820	1.873	4.857	1.541
A-4	3.401	5.818	2.951	1.871	2.333	1.640
A-5	3.206	6.429	3.909	1.830	3.469	1.642
A-6	3.316	6.371	2.591	1.813	3.810	1.596
A-7	3.684	5.887	3.523	1.843	2.578	1.564
mean	3.369	6.080	2.974	1.848	3.673	1.596
s.dev.	0.166	0.243	0.572	0.022	1.265	0.041
%RSD	4.927	3.997	19.23	1.167	34.44	2.569

TABLE 6. COMPARISON OF PERCENT RSD OF DUPLICATE ANALYSES BY XRF

Elements	IDL	Samples G-10	G-20	G-30
Fe	---	57,729	38,321	57,050
		52,947	33,990	58,350
%RSD		4.32	5.99	1.13
Cu	250	1,056	373	726
		919	304	743
%RSD		6.95	10.19	1.15
Zn	200	2,979	449	3,316
		3,022	417	3,490
%RSD		0.73	3.70	2.55
Pb	70	14,943	343	12,138
		14,840	282	11,927
%RSD		0.35	9.76	0.88

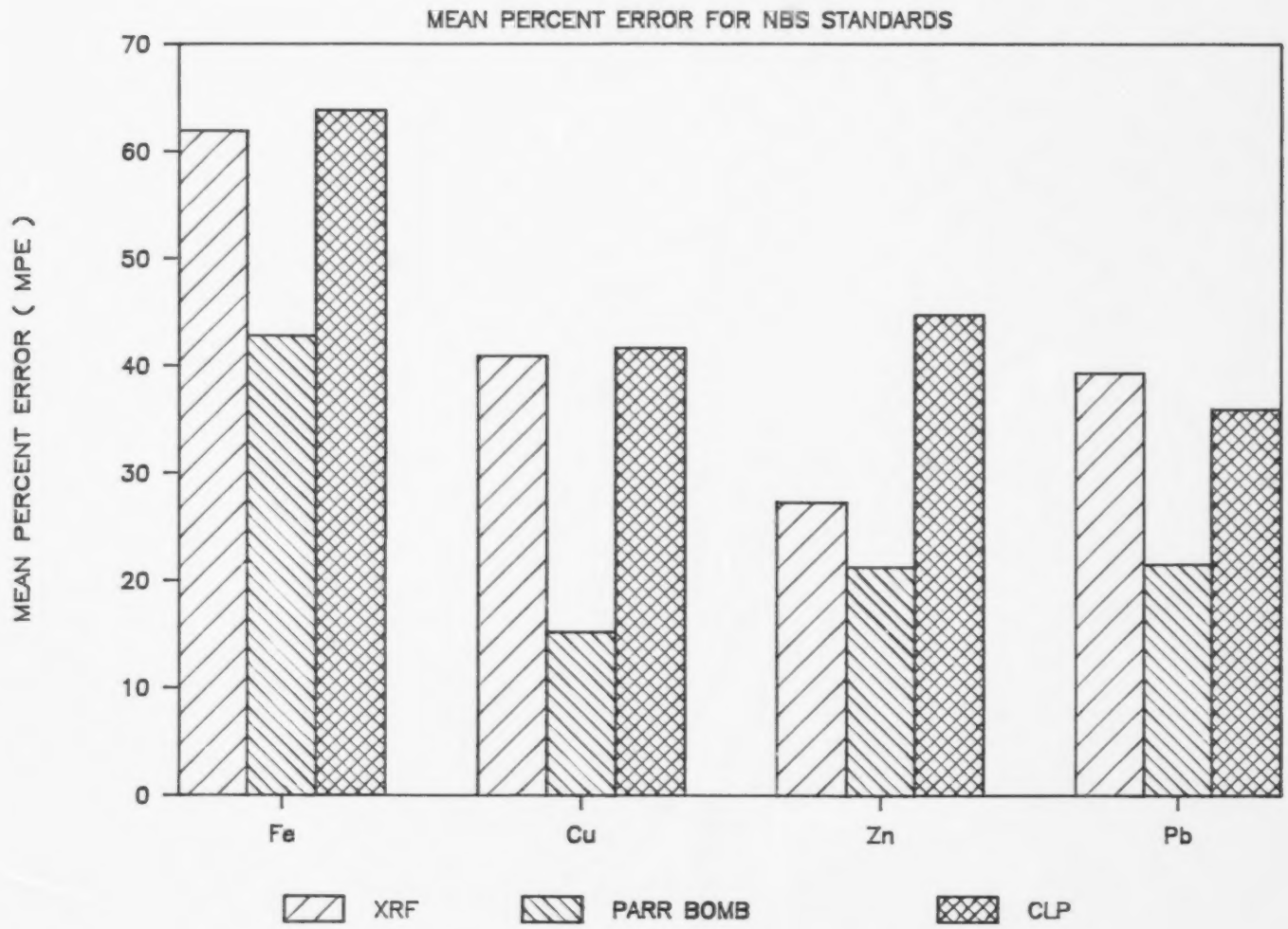

Figure 10. Bar graph of the mean percent error from NBS concntrations.

The NBS certified value is assumed to be the "true" concentration. Each method of analysis recovered concentrations equal to or less than the true concentration for each element. The deviation from the true concentration of each element represents the effect of both bias and lack of precision or MPE for each method. What is interesting to note is that while the Parr bomb method shows the lowest MPE of the three methods, the XRF is within a few MPE of the CLP for Fe, Cu, and Pb. The Zn values for XRF exhibited a lower observed MPE than the CLP values. The overall precision and bias of the results from the CLP and XRF methods are within acceptable scientific limits (±10%).

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